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The electron diffusion coefficient (D_e) for the redox polymer POs-EA, an ethylamine quaternized poly(vinylpyridine) complex of Os(bipyridine)₂Cl₂, has been directly measured by steady-state voltammetry at interdigitated array (IDA) electrodes. In cross-linked POs-EA D_e decreased upon increasing the ionic strength and upon changing the hydrophilic chloride counterion to the hydrophobic perchlorate anion. In 5.0 wt% cross-linked POs-EA D_e is pH dependent increasing from 4.5×10^{-9} to $1.6 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$ as the pyridine rings are protonated. In highly (25 wt%) cross-linked POs-EA, the motion of the chains is restricted, D_e is independent of pH. The results show that D_e increases steeply upon hydration of POs-EA. It is proposed that the extent of electron diffusion in redox hydrogel is determined by segmental motion of the polymer backbone and is therefore enhanced, rather than diminished upon swelling of the redox polymer network, that increases the static distances between redox centers.

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Electron Diffusion Coefficients in Hydrogels Formed of Cross-linked Redox Polymers

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Abstract

The electron diffusion coefficient (D_e) for the redox polymer POs-EA, an ethylamine quaternized poly(vinylpyridine) complex of $\text{Os}(\text{bipyridine})_2\text{Cl}_2$, has been directly measured by steady-state voltammetry at interdigitated array (IDA) electrodes. In cross-linked POs-EA D_e decreased upon increasing the ionic strength and upon changing the hydrophilic chloride counterion to the hydrophobic perchlorate anion. In 5.0 wt% cross-linked POs-EA D_e is pH dependent increasing from 4.5×10^{-9} to $1.6 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$ as the pyridine rings are protonated. In highly (25 wt%) cross-linked POs-EA, the motion of the chains is restricted, D_e is independent of pH. The results show that D_e increases steeply upon hydration of POs-EA. It is proposed that the extent of electron diffusion in redox hydrogel is determined by segmental motion of the polymer backbone and is therefore enhanced, rather than diminished upon swelling of the redox polymer network, that increases the static distances between redox centers.

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Introduction

Redox polymers have been studied for over two decades because of their relevance to electrocatalysis, energy storage and chemical sensors.¹ It was recently shown that redox polymer films in which redox enzymes are immobilized relay electrons between oxidoreductases, such as glucose oxidase, and electrodes.²⁻⁵ An effective electron relaying polymer is poly(4-vinylpyridine) partially complexed with osmium bis(bipyridine) dichloride and quaternized with 2-bromoethylamine (POs-EA).² The dynamic electron-relaying properties of the redox polymers impact on their performance in enzyme electrodes. Realization of high current density, sensitive and miniaturizable enzyme electrodes requires adequately rapid electron diffusion and mass transport to match the maximum function of the ensemble of enzyme molecules. Adequate mass transport can be arrived by using redox hydrogels, where the diffusion coefficients of the substrate and the product may approach those in water. Here we show that hydrogels can be designed to conduct electrons and show that the electron diffusion coefficients in redox hydrogels increase upon swelling and decrease upon dehydration.

The process of electron-relaying through redox polymers is generally considered to involve electron hopping between neighboring redox sites.^{6,7,9-13} The rate determining step for electron diffusion can be electron hopping between neighboring sites on the backbone, segmental motion of the polymer backbone, or macro- and microscopic counterion movement. The controlling factors vary among different redox polymers, and depend on the nature and concentration of the redox species, the flexibility of the polymer backbone and the ionic conductivity of the polymer film. A measure of the ability of a polymer to relay electrons is its electron diffusion coefficient (D_e). In redox polymers D_e has been estimated by transient⁶⁻⁸ and steady-state⁹⁻¹⁴ electrochemical methods. Transient measurements by cyclic voltammetry,⁶ chronoamperometry,^{2f,6} chronocoulometry⁷ and pulse techniques⁸ are affected by interference from charge-compensating macroscopic counterion movement into or out of the polymer network. In steady-state measurements with sandwich electrodes,⁹ rotating ring-disk electrodes¹⁰ and interdigitated array (IDA) electrodes¹¹⁻¹⁴ the interference by ion migration is avoided. In particular, steady-state

voltammetry with IDA electrodes allows the direct measurement of D_e , and does not require knowledge of the film thickness and the concentration of the redox centers in the polymer.¹¹ Additionally, the narrow widths and gaps of the multiple fingers of photolithographically fabricated arrays allow measurement of electron diffusion coefficients in redox polymers that are much lower than the coefficients of diffusion of ions in liquid solutions. For this reason, we measured D_e for POs-EA, cross-linked with poly(ethylene glycol) diglycidyl ether (PEGDE), by steady-state voltammetry with interdigitated array (IDA) electrodes, a method developed by Chidsey et al.¹¹

The principle of steady-state voltammetry at IDA electrodes is the following: When the potential at one of the IDA electrodes is swept from reducing to oxidizing, while the other electrode is maintained at a reducing potential (generator-collector experiment), an anodic steady-state current (I_{ss}) is observed upon redox cycling, because the electrode at the fixed reducing potential generates an oxidizable species. The total charge associated with the redox centers (Q) is obtained by integrating the area of the surface wave voltammogram when the potential of both of the IDA electrodes is scanned (generator-generator experiment). From I_{ss} and Q , D_e is obtained through equation 1.¹¹

$$D_e = (I_{ss}/Q) \text{ gap } (w + \text{gap}) (N/[N-1]) \quad (1)$$

The attractive feature of this method is that D_e is derived solely of I_{ss} , Q and the IDA geometry.

Here we report the steady-state voltammetric characteristics of POs-EA/PEGDE hydrogel films on IDA electrodes. We find these to depend on the parameters that control swelling, i.e. on the ionic strength, the anion, pH and the extent of cross-linking. We then compare the dynamics of charge transport in this redox epoxy polymer network with those for earlier studied redox polymer systems.^{2f,6,7} We conclude that our finding that swelling of the gel enhances electron transport is consistent with the earlier proposed mechanism of electron transport in redox polymers, involving motion of segments of the polymer backbone.

Experimental Sections

Chemicals. POs-EA was prepared as described.^{2f} The polymer consists of 50 kDa polyvinylpyridine (PVP) partially complexed with Os(bpy)₂Cl₂ (Os), and quaternized with 2-bromoethylamine (EA). The PVP/Os/EA ratio of the polymer studied was 6:1:1.2. The diepoxide used for cross-linking the polyamine was poly(ethylene glycol)diglycidyl ether (Polyscience, PEG400). The electrolyte solution was 20 mM phosphate buffer at pH 7.0, containing 0.1 M NaCl. All chemicals were reagent grade and were used without further purification.

Apparatus. The experiments were performed by using a Pine Instruments RDE-4 bipotentiostat with a x-y-y' Kipp and Zonnen recorder. The single-compartment water-jacketed electrochemical cell had Pt auxiliary and saturated calomel electrode (SCE) reference electrodes. The experiments were carried out under N₂ at room temperature (20 ± 1°C).

IDA electrodes. The IDA electrodes were fabricated by conventional photolithography using a positive photoresist (Hoechst, AZ 1350J-SF) and sputter-deposition of gold onto the chromium primed glass substrate. Detail of the procedure were described in previous papers.^{15,16} The electrodes consisted of 100 (N), 5.0 μm wide fingers (w), separated by 5.0 μm gaps (gap), that were 2.0 mm long. Except for the finger area the electrode was covered with the photoresist. Prior to coating the redox polymer onto the IDA electrode, the electrode was cleaned in hot nitric acid solution. Cyclic voltammograms for 2.0 mM ferrocenecarboxylic acid were obtained at a 5.0 mV/sec scan rate. The voltammogram shape, steady-state current and the collection efficiency were as predicted by theory.¹⁷

5.0 wt% cross-linked POs-EA polymer coated on the IDA electrodes were prepared by pipetting premixed solutions of 20 mL POs-EA (5.0 mg/mL) and 2.5 mL PEGDE (2.0 mg/mL) onto the both finger and internal gap areas and allowing the solvent to evaporate at room temperature. The electrodes were then left to cure in the air for 24 hr.

In the generator-collector experiments, the cyclic voltammograms were obtained by scanning the potential of the generator from 0.0 V to 0.6 V vs SCE at various scan rates, while maintaining the potential of the collector at 0.0 V vs SCE. In the generator-generator experiments, the

voltammograms were obtained by scanning the potentials of both of the IDA electrodes from 0.0 V to 0.6 V vs SCE at various scan rates. Diffusion limited steady-state currents were observed at 0.6 V vs SCE. At this potential the oxidative current for the $[\text{Os}(\text{bpy})_2\text{vpyCl}]^+$ ion were diffusion limited.

RESULTS AND DISCUSSION

Electrochemical behavior. Figure 1 shows the cyclic voltammograms for POs-EA cross-linked with 5.0 wt% PEGDE at various scan rates. The voltammograms of the generator-generator experiment are represented by the dotted lines. The voltammograms exhibited well-defined surface waves at both IDA electrodes. The waves were symmetrical and the peak currents were close to being proportional to the scan rate. The $[\text{Os}(\text{bpy})_2\text{vpyCl}]^+$ centers in the polymer were completely oxidized both on the fingers and in the internal gaps. The charge of the POs-EA polymer coated IDA electrodes (Q) was calculated by integrating the currents of the voltammograms. The values of Q were identical at the different scan rates. Their $Q = 9.26 \text{ mC}$ value corresponded to an $[\text{Os}(\text{bpy})_2\text{vpyCl}]^{+/2+}$ coverage of $9.60 \times 10^{-9} \text{ mol cm}^{-2}$.

The voltammograms in generator-collector experiments (solid lines) exhibited steady-state currents at 0.6 V vs SCE, where the current was diffusion limited for $[\text{Os}(\text{bpy})_2\text{vpyCl}]^+$. The generator electrode voltammograms differed from those of the collector electrodes. Their collector electrode voltammograms had a sigmoidal shape at any scan rate. However, those at the generator electrodes depended on the scan rate. The voltammogram at the generator electrode represented the sum of that at the collector electrode and that in the generator-generator experiments. Thus, when the peak current in the generator-generator experiment reached a substantial fraction of the steady-state current, the voltammogram showed a peak (Figure 1A, B). However, when the peak current was small relative to the steady-state current, the voltammogram had the sigmoidal shape seen in Figure 1C. The steady-state current showed the expected $[\text{Os}(\text{bpy})_2\text{vpyCl}]^+$ oxidation at the generator, transport of electrons through the redox polymer (by electron hopping or electron self-exchange between neighboring Os^{3+} and Os^{2+} sites) and re-reduction of $[\text{Os}(\text{bpy})_2\text{vpyCl}]^{2+}$ sites

at the collector (so called redox cycling). The anodic limiting current was identical with the cathodic one, and the limiting current was independent of scan rate. The observed hysteresis between forward and backward potential-swept voltammograms at the collector electrode was caused by inadequate time for establishment of steady-state concentration profiles at the applicable scan rates. Thus, the hysteresis decreased as the scan rate decreased. The results indicate the existence of a linear concentration gradient in the $\text{Os}^{2+}/\text{Os}^{3+}$ ratio between the generator and the collector electrodes, and establish that charge transport through the POs-EA polymer limits the current. Using equation 1, the value of D_c was calculated to be $1.6 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$ at pH 2.89.

Effect of the ionic strength and the anionic species on D_c . The voltammograms of Figure 2 revealed a strong ionic strength dependence of D_c . When the concentration of NaCl was changed from 0.1 M to 1.0 M, Q remained constant but I_{ss} decreased. Moreover, when the potential of one IDA electrode was swept, while the other of IDA electrode was disconnected (generator-open circuit experiment, dashed line), a shoulder, indicating lateral electron diffusion between the fingers was seen. This shoulder was sharp in 0.1 M NaCl; that in 1.0 M NaCl had, however, a diffusional tail. The relationship between D_c and the NaCl concentration is shown in Figure 3A. D_c decreased linearly upon increasing the concentration of NaCl above 0.1 M. Below 0.1 M NaCl, D_c appeared constant, because the ionic strength was controlled by the 20 mM phosphate concentration. This result contrasts earlier ones^{2f,6b} obtained by transient methods. Evidently, ion migration effects can not be ignored at low ionic strengths in the transient measurements. They do not effect, however, the steady-state measurements, where there is no net movement of ions into or out of the films. The results show that D_c decreases with increasing with the ionic strength. Evidently, dehydration upon increasing the ionic strength made the cross-linked structure more rigid. The relationship between the half-wave potential ($E_{1/2}$) and the concentration of NaCl is shown in Figure 3B. $E_{1/2}$ was shifted in the cathodic direction with increasing the concentration of NaCl by 20 mV per decade. This is in accordance with the previous results^{2b,f} and results on another redox polymer system.¹⁸ The 20 mV per decade slope shift in half wave

potential, that was well below the theoretical 60 mV, suggests formation of a complex or salt between the $[\text{Os}(\text{bpy})_2\text{vpyCl}]^{+/2+}$ centers and the chloride anion.

Figure 4 shows the cyclic voltammograms at the IDA collector electrodes at 0.1 M NaCl (A) and 0.1 M NaClO₄ (B). When the hydrophilic chloride anion is replaced by the hydrophobic perchlorate anion, the steady-state current decreases in the generator-collector experiment. The peak current also decreased and a diffusional tail appeared in the generator-generator experiment, showing that the electron transport was now sluggish. Such an effect was also observed in other redox polymer films.^{6b,7,9g} Apparently, the polymer structure becomes more rigid through hydrophobic interactions of the perchlorate anion that is less hydrated than the chloride anion. Although microscopic counterion transport is often considered as the rate determining step in electron transport in polymers, the observed decrease in D_c at increasing ionic strengths does not support such a model. Because the Stokes radius of the chloride anion is almost identical with that of perchlorate anion¹⁹, the polymer structure need not be changed for geometrical considerations upon substitution of the anions, and, therefore, the distance between the $\text{Os}^{2+}/\text{Os}^{3+}$ sites should be the same with either chloride or perchlorate as counterion. The anion changes, however, the very nature of the polymer, because hydrophobic interactions are enhanced when perchlorate replaces the chloride anion. Correspondingly, the half-wave potential of POs-EA in 0.1 M perchlorate was shifted by 40 mV in the cathodic direction to 0.245 V vs SCE. This shift resulted from a change in either the formation constant of the complex between the $[\text{Os}(\text{bpy})_2\text{vpyCl}]^{+/2+}$ cation and the monovalent anion i.e. the local dielectric constant or in the solubility of the oxidized redox salts which was also affected by the local dielectric constant.^{18d,20,21} Evidently, in the hydrophobic system the complex that was formed was stronger.

Dependence of D_c on pH. Figure 5 shows the dependence of the cyclic voltammograms for the collector of the IDA electrode on pH. The steady state current decreased with increasing pH. However, the total charge was constant at any pH. The pH dependence of D_c for POs-EA cross-linked with 5.0 wt% PEGDE calculated by the equation 1 is shown in Figure 6. D_c changes remarkably near pH 4, close to the pK_a of the pyridine nitrogen, from 4.5×10^{-9} to 1.6×10^{-8}

$\text{cm}^2 \text{s}^{-1}$, as was earlier also by chronoamperometry.^{2f} When the pyridine nitrogen of the POs-EA polymer was protonated at lower pH and the more positively charged gel expanded, the concentration of the Os sites decreased. The increase in D_e upon protonation implies that the rate determining step for electron transport through the POs-EA polymer is not electron hopping. According to the hopping theory²², D_e decreases upon decreasing the concentration of redox sites as shown in the equation 2.

$$D_e = k_{ex} d^2 C / 6 \quad (2)$$

where k_{ex} is the electron self-exchange rate constant, which for the couple considered is independent of pH, and d is the average distance between neighboring osmium sites.²³ Evidently the polymer film is swollen and the backbone of the polymer is flexible when the pyridines are protonated at a pH below pK_a , where D_e is high. The increase in D_e with the swelling of the cross-linked POs-EA polymer is consistent with control of the electron diffusion by segmental motion of the polymer backbone.

The voltammograms in the generator-generator experiments (dotted lines) also changed with pH. The peak currents increased with pH and the peaks' width at half-height narrowed. The values of the peak currents and the peak widths at half-height are summarized in Table I. At pH 2.0 the peak current and the peak width in the anodic voltammetric wave were identical with their theoretical values.²⁴ However, the anodic peak current and the peak width deviated from their theoretical values at high pH. This deviation is explained by interaction between the redox species, as observed earlier in other polymers.^{1,25,26} When the pyridine nitrogen of the POs-EA polymer is protonated and the polymer is swollen at pH 2.0, the distance between Os sites is large and the sites do not interact. Thus, the voltammogram of the POs-EA polymer film is that characteristic for an adsorbate on an electrode, the adsorption of which is well described by a Langmuir isotherm. Because at higher pH the pyridine nitrogens are not protonated, the polymer is less swollen and the distance between the Os sites is small enough for the sites to interact. Now the voltammogram has the characteristics of adsorption represented by the Frumkin isotherm. The behavior of the

cathodic waves is, however, characteristic of Langmuir isothermal adsorption at any pH, because the more highly charged oxidized redox polymer is more swollen than the reduced redox polymer.

The D_e values for the POs-EA polymer at various cross-linker concentrations are summarized in Table II. For the network made with 5.0 wt% cross-linker D_e was pH dependent. D_e was, however, almost independent of pH for the polymer made with 25 wt% cross-linker. When the concentration of the cross-linker is 25 wt%, 32 % of the pyridines in the polymer are cross-linked with the diepoxide. At such extreme cross-linking the polymer can not swell even at low pH, and the electron-transfer controlling segmental motion of the polymer backbone is severely restricted.

We conclude that in cross-linked POs-EA the electron diffusion coefficients increase upon hydration of the redox polymer network and that electron transport through the network is controlled by segmental motion of the polymer backbone, not by electron exchange between neighboring redox sites of a chain nor by macroscopic or microscopic counterion transport. The D_e measurements, are relevant to the design of hydrogels that electrically connect redox centers of enzymes to electrodes. They are being extended to hydrogels made with redox polymer networks to which enzymes are covalently bound.

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Figure 1. Scan rate dependence of the cyclic voltammograms for POs-EA cross linked with 5.0 wt% PEGDE coated on IDA electrodes, at an $[\text{Os}(\text{bpy})_2\text{vpyCl}]^{+/2+}$ site coverage of $\Gamma = 9.60 \times 10^{-9} \text{ mol cm}^{-2}$ in 20 mM phosphate buffer at pH 2.89 containing 0.1 M NaCl. Generator-collector (solid line), generator-generator (dotted line) voltammograms are shown for (A), 5.0; (B), 2.0; (C), 1.0 mV sec^{-1} .

Figure 2. Ionic strength dependence of cyclic voltammograms for POs-EA cross-linked with 5.0 wt% PEGDE coated on IDA electrodes, at an $[\text{Os}(\text{bpy})_2\text{vpyCl}]^{+/2+}$ site coverage of $\Gamma = 1.93 \times 10^{-8} \text{ mol cm}^{-2}$ in 20 mM phosphate buffer at pH 7.0 and at 1.0 mV s^{-1} scan rate. Generator-collector (solid line), generator-open circuit (dashed line), generator-generator (dotted line) voltammograms are shown for (A), 0.1 M; (B), 1.0 M NaCl.

Figure 3. Effect of the ionic strength on the electron diffusion coefficient (A) and the half-wave potential of the POs-EA polymer (B). The conditions are the same as in Figure 2.

Figure 4. Anion dependence of the cyclic voltammograms at the collector electrode for POs-EA cross-linked with 5.0 wt% PEGDE, at an $[\text{Os}(\text{bpy})_2\text{vpyCl}]^{+/2+}$ site coverage of $\Gamma = 4.01 \times 10^{-9} \text{ mol cm}^{-2}$ in 20 mM phosphate buffer at pH 7.0 and at 2.0 mVsec^{-1} scan rate. Generator-collector (solid line), generator-generator (dotted line) voltammograms are shown for (A), 0.1 M NaCl; (B), 0.1 M NaClO_4 .

Figure 5. pH dependence of the cyclic voltammograms at the collector for POs-EA cross-linked with 5.0 wt% PEGDE, at an $[\text{Os}(\text{bpy})_2\text{vpyCl}]^{+/2+}$ site coverage of $\Gamma = 4.35 \times 10^{-9} \text{ mol cm}^{-2}$ in 20 mM phosphate buffer containing 0.1 M NaCl and at 2.0 mV sec^{-1} scan rate. Generator-collector (solid line), generator-generator (dotted line) voltammograms are shown for pH (A), 2.0; (B), 4.0; (C), 7.0.

Figure 6. pH dependence of the electron diffusion coefficient of POs-EA cross-linked with 5.0 wt% PEGDE, $\Gamma = 4.35 \times 10^{-9} \text{ mol cm}^{-2}$ in 20 mM phosphate buffer containing 0.1 M NaCl at 2.0 mV s⁻¹ scan rate.

Table I. pH Dependence of the Peak Current and the Peak Width at Half-Height of the Anodic and the Cathodic Waves

pH	peak current, nA		peak width, mV	
	anodic	cathodic	anodic	cathodic
2.0	80	72	90	95
4.0	84	72	85	95
5.0	88	68	80	90
7.0	100	72	75	90
theoretical	80 ^a		90.6	

a, value calculated from $\Gamma = 4.35 \times 10^{-9} \text{ mol cm}^{-2}$, $v = 2.0 \text{ mV sec}^{-1}$.

Table II. Effect of the Extent of Cross Linking on the Electron Diffusion Coefficient (D_e)

Cross linker wt%	$D_e, \text{ cm}^2 \text{ s}^{-1}$	
	pH 3.0	pH 7.0
5	1.6×10^{-8}	4.5×10^{-9}
25	4.2×10^{-9}	3.2×10^{-9}

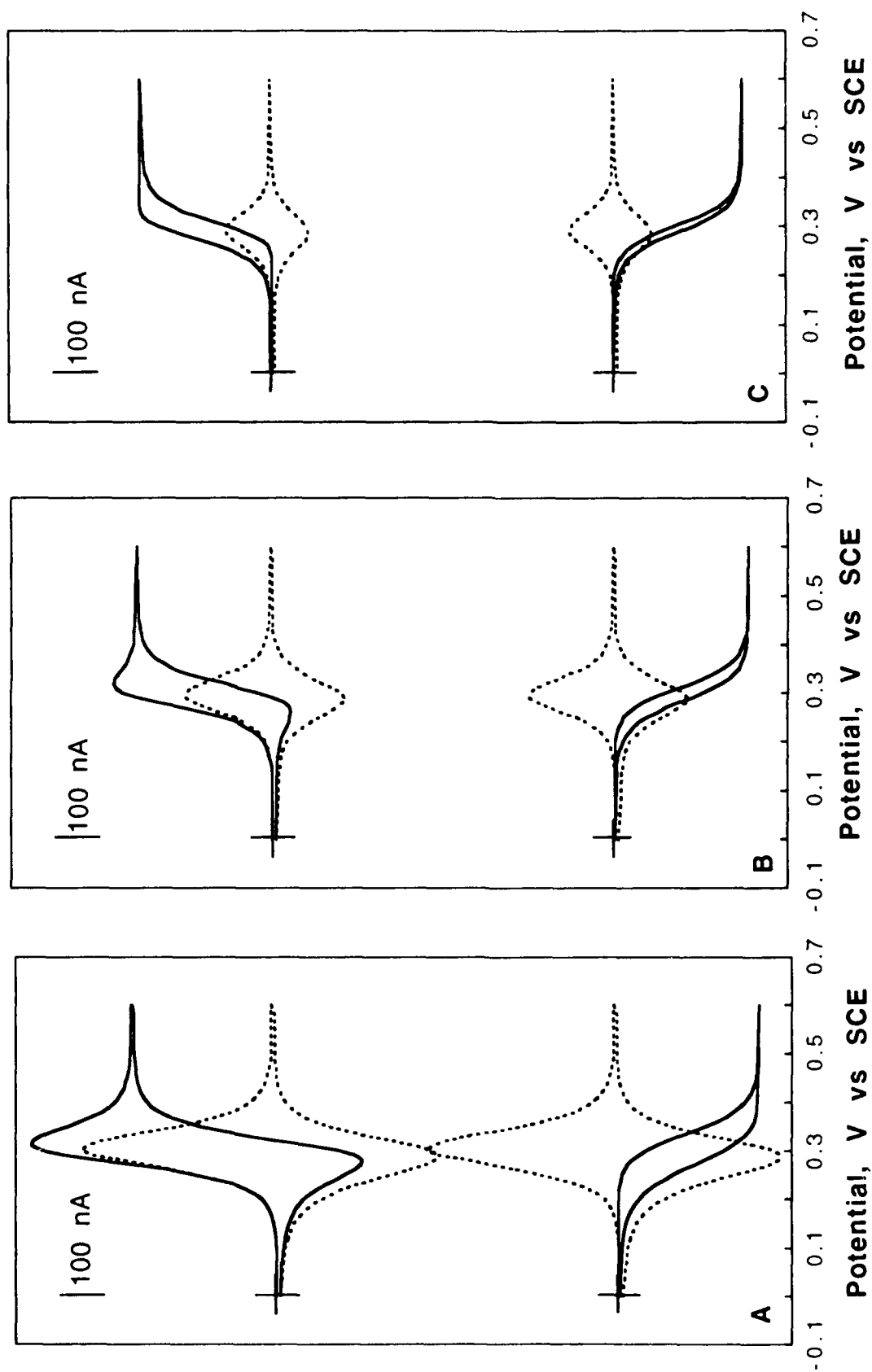


Figure 1. A.Aoki et al.

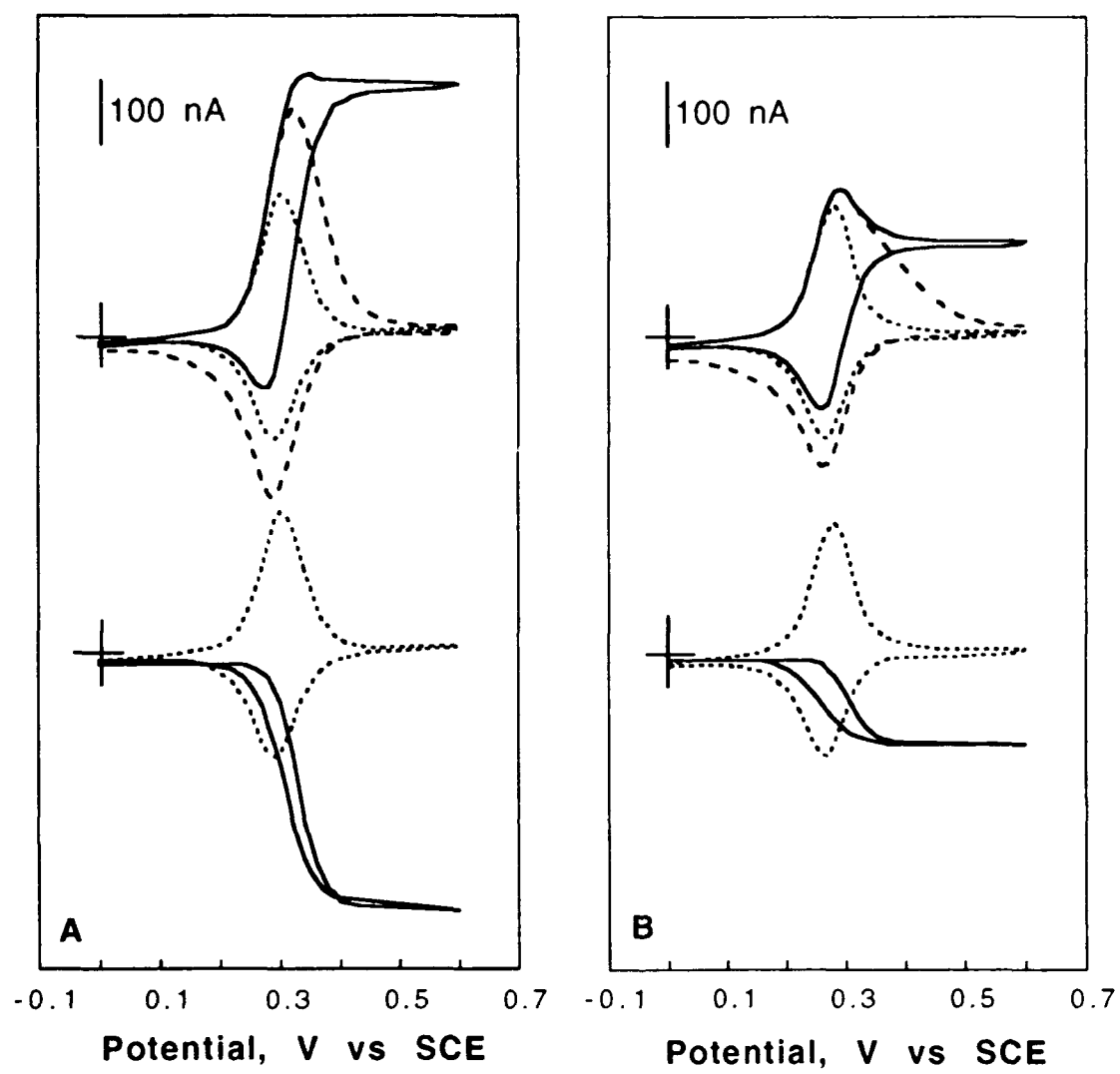


Figure 2. A.Aoki et al.

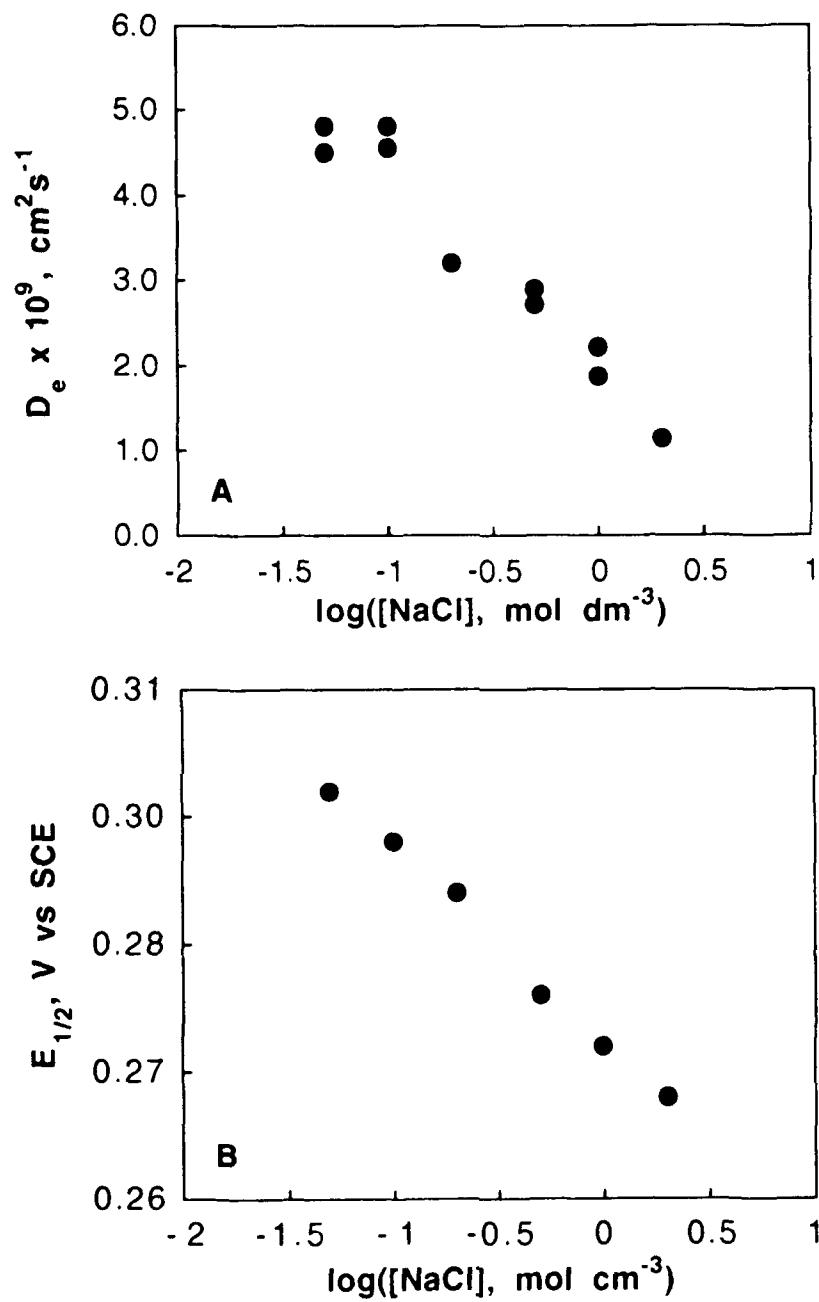


Figure 3. A.Aoki et al.

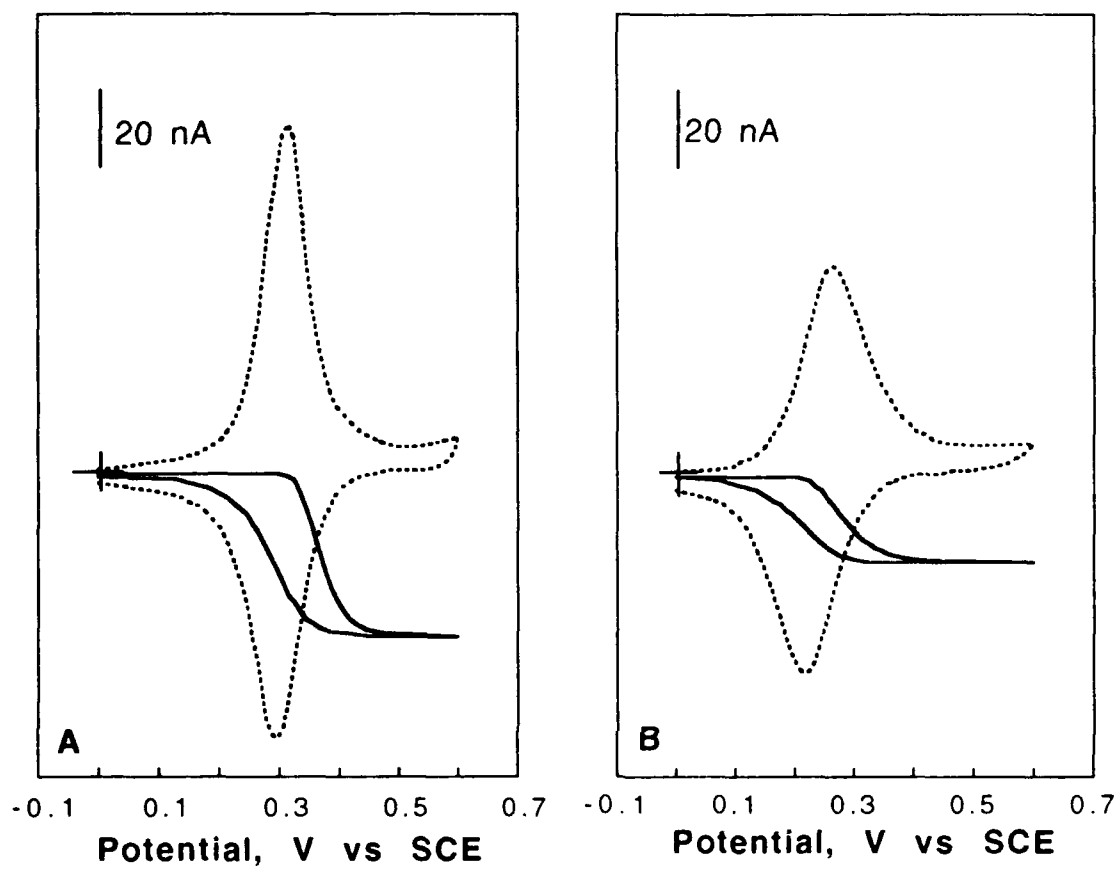


Figure 4. A.Aoki et al.

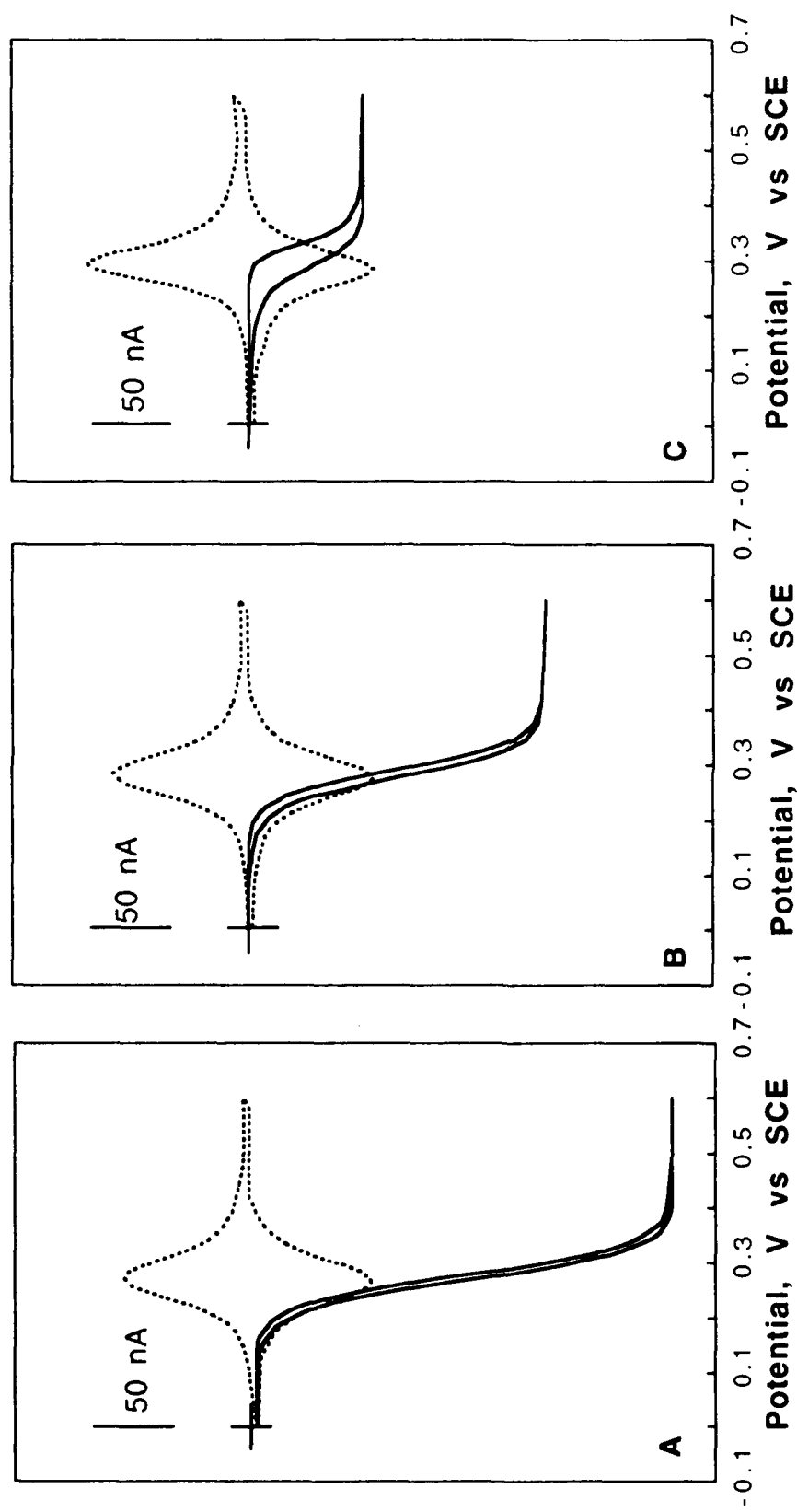


Figure 5. A.Aoki et al.

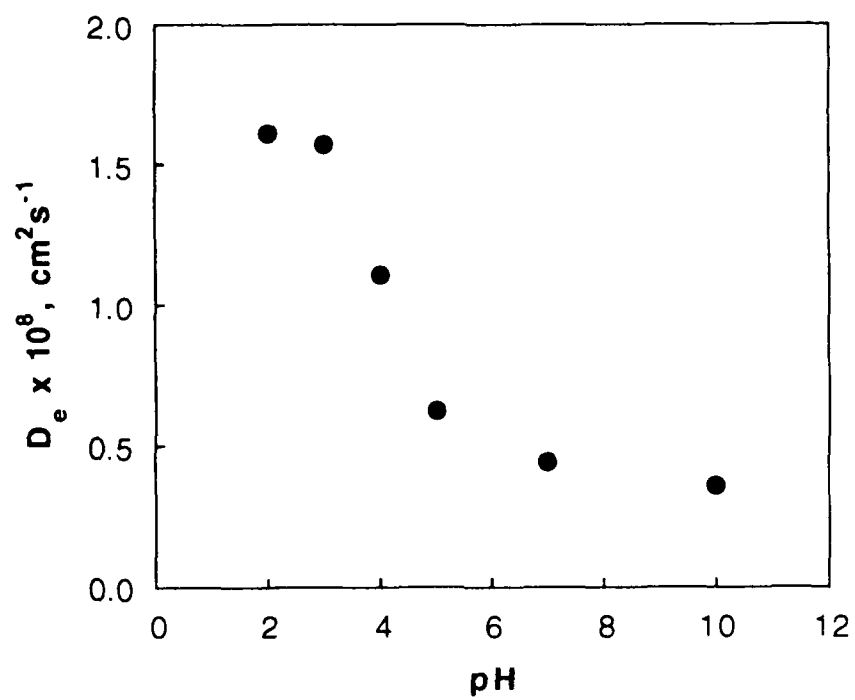


Figure 6. A.Aoki et al.